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INTERACTION OF THE DIBORIDES OF TITANIUM, ZIRCONIUM, AND HAFNIUM WITH CARBON

Yu. V. Levinskiy and S. Ye. Salibekov

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ABSTRACT

The extent to which the compositions of TiB_2, ZrB_2, and HfB_2 are modified or otherwise affected by carbon is investigated experimentally at temperatures up to melting, in order to assess the effects of contact with carbon (graphite) in special devices or technological applications wherein such contact is required. The systems are prepared by direct synthesis and by the borocarbide process. The eutectic temperatures, eutectic compositions, and hypothetical state diagrams are determined for these systems. The formation of new solid phases and hence the solubility of carbon in the diborides are found to be negligible. The investigated mixtures are confirmed to be pseudobinary systems.

Author

Titanium diboride TiB_2, zirconium diboride ZrB_2, and hafnium diboride HfB_2 /588* have melting points of 3253 ± 100, 3313 ± 100, and 3523 ± 100°K, respectively (ref. 1), and along with graphite are among the most refractory of materials. In present-day high-temperature engineering, it is often necessary to deal with contact interaction between the borides and graphite. Examples of this include boride-graphite thermocouples (ref. 2), high-temperature furnaces, technological processes for the preparation of borides and various products utilizing them. This places considerable importance upon the investigation of borides and their interaction with graphite.

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*Numbers in the margin indicate pagination in the original foreign text.

There are indications in the literature that the diborides of titanium, zirconium, and hafnium do not interact with carbon (ref. 3). Furthermore, it has been established that the systems MeB_2-C (where Me stands for titanium, zirconium, or hafnium) are pseudobinary (refs. 4 and 5). However, none of the papers devoted to the investigation of interaction in these systems make any mention of the solubility of carbon in the borides, the behavior of the state diagrams, or the melting temperatures.

In the work described herein, we investigated the interaction of the diborides of titanium, zirconium, and hafnium with carbon from the point of view of the solubility of carbon in the borides and the appearance of liquid phases in the systems MeB_2-C.

For the investigation of the solubility of carbon in the borides, an extremely important factor is the purity of the initial products, especially the borides. Of course, the borocarbide method (ref. 3) has found the most widespread application for the preparation of diborides; this method is based on the reaction

$$MeO + B_4C + C \rightarrow MeB_2 + CO$$

Borocarbide processes take place at temperature of the order 2000 to 2200°K. If the diborides of titanium, zirconium, and hafnium have a high carbon solubility, one might expect that, under the conditions attendant upon borocarbide processes, borides containing a definite quantity of carbon would be obtained.

Diborides can also be obtained by synthesis of the initial elements under conditions that preclude carbon contamination of the final product.

We prepared and investigated titanium, zirconium, and hafnium diborides by both methods.

For the initial materials in the borocarbide method, we used powdered titanium oxide containing 0.01% Fe and 0.05% Cu, powdered zirconium oxide containing 0.03% Al_2O_3, 0.05% HfO_2, 0.3% CaO, 0.1% Fe_2O_3, 0.3% SiO_2, 0.2% MgO, and 0.02% TiO_2, and powdered boron carbide containing B_2O_3 and C impurities and carefully roasted carbon black with an ash content of less than 0.05%.

For the initial materials in the diboride synthesis process, we used powdered titanium containing 0.04% C, 0.11% Si, 0.1% Ni, 0.05% N, 0.05% Al; zirconium containing 0.02% Al, 0.05% Hf, 0.05% Fe, 0.01% Mg, 0.1% Si, 0.005% Ti; and hafnium containing 2.8% Zr, 0.05% Fe, 0.01% Mg, 0.07% Si, 0.009% Ti.

The mean grain size of the powdered metals was 5 to 10 nm. The boron used in synthesis had impurities of 0.0036% Si, 0.00036% Fe, 0.01% Cu, 0.0003% Mg, 0.0006% Pb, and 0.0004% Al.

The titanium and zirconium diborides were prepared by the borocarbide process under conditions described in the literature (ref. 3).

For synthesis of the diborides, the powdered metal and boron were mixed in stoichiometric proportion, formed into pellets, and heated in a vacuum kiln with a tungsten heater at a temperature of 1800°K for one hour.

The boride powders prepared by both methods were subjected to x-ray /589
analysis. Phase x-ray analysis, performed on the URS-50I instrument with copper emission, revealed in every case the presence of only one phase, titanium, zirconium, or hafnium diboride. To determine the lattice parameters, we made x-ray photographs with a KROS-1 camera using copper emission. The parameters were calculated for TiB_2 from the lines [301], [212], [203], [004], for ZrB_2 from the lines [302], [220], [213], and for HfB_2 from the lines [104], [302], [220].

The lattice parameters of titanium diboride prepared by the borocarbide process and by synthesis turned out to be equal, respectivelay, to:

a = 3.02 ± 0.01 kX, c = 3.21 ± 0.05 kX, and a = 3.04 ± 0.01 kX; c = 3.15 ± 0.05 kX; for zirconium diboride: a = 3.167 ± 0.002 kX, c = 3.518 ± 0.005 kX; a = 3.169 ± 0.002 kX, c = 3.511 ± 0.005 kX. The lattice parameters of HfB_2 prepared by synthesis of the elements were: a = 3.138 ± 0.002 kX, c = 3.468 ± 0.005 kX.

The solubility of carbon at high temperatures was investigated and the temperatures for the onset of the liquid phase determined in the systems MeB_2-C in a vacuum apparatus.

The powdered titanium, zirconium, and hafnium diborides synthesized from the elements were placed in the hollow of a graphite tube with an outside diameter of 8 mm and hollow diameter of 2 mm. The length of the tube was 80 mm. The middle section of the tube was scraped down in order to diminish its cross section. The tube, packed with the powder, was secured in the contacts of the vacuum apparatus. After creating a vacuum of $\sim 10^3$ mm Hg, the tube was heated by passing current directly through it. The temperature was measured by an optical pyrometer. The readings of the pyrometer included corrections for the emission coefficient of graphite. After keeping at the given temperature for a definite period, the current was turned off and the tube quickly cooled (the temperature dropping approximately 1000°C in the first ten seconds). After cooling, the tube was taken out and the boride contents subjected to x-ray analysis and, in the case of melt formation, microstructural analysis.

The melt formation temperature was considered to be the lowest temperature at which a bead was observed in the hollow of the opened tube.

Titanium diboride melted in contact with graphite at a temperature of 2560 ± 30°K, zirconium diboride at 2500 ± 30°K, hafnium diboride at 2610 ± 30°K. It should be noted that, although the absolute error in measuring the temperature

was 30°, the melting temperature was reproduced within 10° in repeated tests.

X-ray phase analysis disclosed that below the temperatures at which the liquid phase was formed, as well as at higher temperatures, only two phases exist in the systems TiB_2-C, ZrB_2-C, and HfB_2-C: the corresponding diboride and carbon.

X-ray photographs taken from the melts of MeB_2-C pounded into powders yielded the following values for the lattice parameters of the boride phases: TiB_2: a = 3.00 ± 0.01 kX, c = 3.22 ± 0.05 kX; ZrB_2: a = 3.160 ± 0.002 kX, c = 3.528 ± 0.005 kX; HfB_2: a = 3.136 ± 0.002 kX, c = 3.471 ± 0.005 kX.

Photographs of slices prepared from the molten samples are shown in figure 1. The melts of all three systems have a distinct eutectic structure, consisting of graphite and the corresponding boride. The composition of the eutectics was determined from slices by the planimetric method described in reference 6. The relative amount of the phases was measured on an IZA-2 comparator. A total of at least 500 measurements were made for the eutectic composition of each system. It was thus established that the eutectics in the systems TiB_2-C, ZrB_2-C, and HfB_2-C contain 15, 19, and 24 mol.% diboride, respectively.

It follows from the experimental data that the solubility of carbon in the diborides of titanium, zirconium, and hafnium is very slight, since the diborides prepared by different methods, as well as diborides heated with carbon above the eutectic temperatures in the corresponding systems MeB_2-C have, within the limits of experimental error, the same lattic parameters.

When the diboride-carbon mixtures were heated to different temperatures, /590 right up to the melting point, the onset of new solid phases was not detected in any of the systems. Consequently, the investigated MeB_2-C systems are pseudobinary, which is in agreement with the earlier literature.

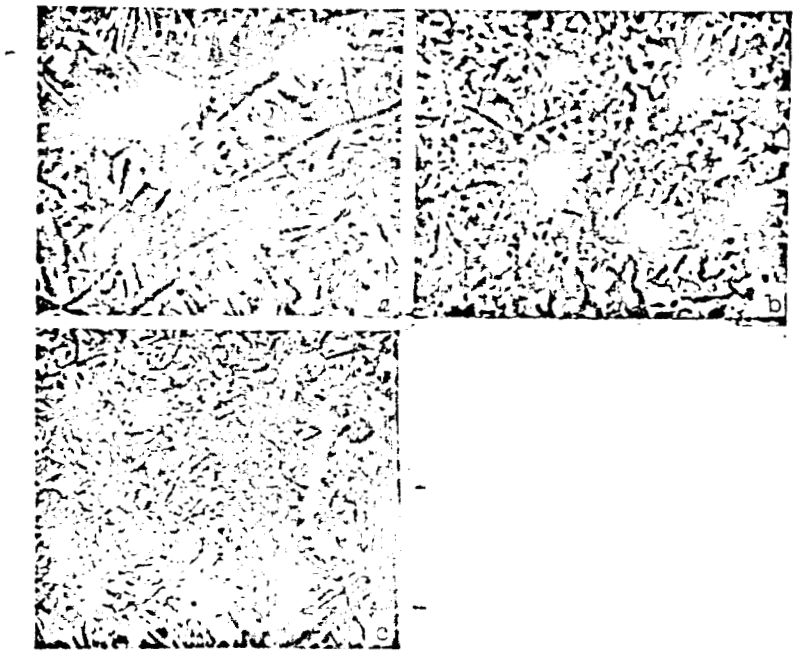

Figure 1. Photographs of Eutectics in the Systems TiB_2-C (a); ZrB_2-C (b); HfB_2-C (c); (X 200).

It is apparent from the photographs of the sections of melted mixtures that all three of the systems investigated have a eutectic nature. Bearing in mind that values obtained for the eutectic temperatures and the eutectic composition, as well as the absence of any appreciable solubility of carbon in the diborides, hypothetical diagrams of the systems TiB_2-C, ZrB_2-C, and HfB_2-C were constructed, as shown in figure 2.

The information gained herein on the interaction of titanium, zirconium, and hafnium diborides with carbon motivate the conclusion that the presence of carbon in all phases of operation with these borides will not significantly affect the latter. Hence it follows that the borocarbide method is completely /591 acceptable as a process for obtaining pure borides. All technological operations for the preparation of finished products utilizing the powdered borides can be carried out in the presence of carbon, i.e., hot pressing in graphite forms and sintering in graphite tube ovens can be applied to these materials

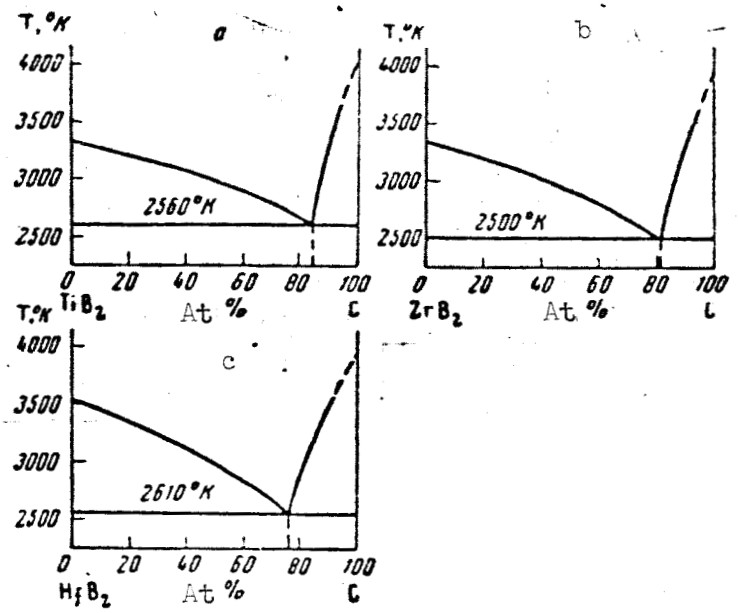

Figure 2. Hypothetical State Diagrams of the Systems TiB_2-C (a); ZrB_2-C (b); HfB_2-C (c).

without danger of altering their composition. Diboride products in contact with graphite, for example, high-temperature boride-graphite thermocouples can function safely to temperatures 2500°K without interacting with the external medium.

CONCLUSIONS

1. It has been established that the solubility of carbon in the diborides of titanium, zirconium, and hafnium at high temperatures is inconsequential.

2. It has been confirmed , ZrB_2-C, and HfB_2-C are pseudobinary systems.

3. The eutectic temperatures and compositions have been ascertained in the systems TiB_2-C, ZrB_2-C, and HfB_2-C and their hypothetical state diagrams have been presented.

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